SOME SUBSTITUTED BETA-PHENYL ACROLEINS AND THEIR REDUCTION PRODUCTS

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science,
of Columbia University.

BY

GARFIELD POWELL, M.A., M.Sc.

L. C.

NEW YORK CITY
1930

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INTRODUCTION

The work described below was undertaken as a study of the alpha-alkyl substituted cinnamic aldehydes, including such cinnamic aldehydes further substituted in the benzene nucleus with alkoxy or alkyl groups, and the reduction products theoretically derivable from them by hydrogenation of the $-CH=CR\cdot CHO$ group common to all of them. These reduction products would comprise a saturated aldehyde $-CH_2CHR\cdot CHO$, an unsaturated alcohol $-CH=CR\cdot CH_2OH$, a saturated alcohol $-CH_2CHR\cdot CH_2OH$, a propene $-CH=CR\cdot CH_3$, and a propane $-CH_2CHR\cdot CH_3$. Only a few of such unsaturated aldehydes have been described in the literature[3, 45] and they have not been described as a class. Of the reduction products, also, only a small number has been described, in the course of work in other directions[18, 42, 11, 21] and this number includes no unsaturated alcohols and but one saturated aldehyde, the propanes being the best known. The alpha-unsubstituted representatives of all these classes are all more or less odoriferous and among them lie some of the most valuable perfume bodies (cinnamic alcohol, cinnamic aldehyde, safrole, etc.). The alpha-substituted bodies might therefore well be expected to be odoriferous also. For the preparation of some of the reduction products the method of catalytic hydrogenation by the method of Skita was employed as a synthetic method over the whole series, a method formerly employed for representatives of groups rather than homologues or closely related individuals, and one whose value in synthetic work of this sort has not previously been tested. Thus in the case of cinnamic aldehyde itself, the only one formerly reduced by this method, the behavior has been disputed ([23] compare [45]) on hydrogenation in identical circumstances. For the preparation of the unsaturated alcohols the method of reduction with

ethyl alcohol and metal alcoholate from the unsaturated aldehyde was used and it is worthy of note that by this method a monomolecular "cubebin" was one of the unsaturated alcohols prepared, of importance in itself in relation to natural "cubebin," having been previously sought and claimed erroneously by others. The preparation of the propenes was not attempted. The classes were studied comparatively in respect of odor, in particular as to the effects of homologous substitution at the double bond. It is known that in some cases among the unsaturated aldehydes there are profound differences among homologues substituted at the double bond, and a comparison among the classes and individuals prepared showed such change to be abnormal. The behavior of the unsaturated aldehydes on catalytic reduction by the method of Skita showed a production in all cases of non-ethylenic substances (compare [23] and [35]), no ethylenic bodies being observed, and showed the method to be confidently applicable for the production of saturated aldehyde, alcohol and propane from each aldehyde, with no great trouble of manipulation or control for each case. The work is thus a study of the unsaturated aldehydes of the mentioned types in respect of their reduction by the method of Skita, their preparation, and properties in some other respects, and in respect of their odor in the particular of homologous substitution at the double bond, this latter by comparison with some corresponding unsaturated alcohols and non-ethylenic bodies similarly substituted in the same position (the alpha position to the aldehyde group).

FLOW SHEET

R	Unsaturated Aldehyde	Saturated Aldehyde	Unsaturated Alcohol	Saturated Alcohol	Propane
C_6H_5—	$RCH{=}CEt{\cdot}CHO$	$RCH_2CHEt{\cdot}CHO$ (9) New	$RCH{=}CEt{\cdot}CH_2OH$ (27) New	$RCH_2CHEt{\cdot}CH_2OH$ (14a)	$RCH_2CHEt{\cdot}CH_3$ (20a)
	$RCH{=}CAm{\cdot}CHO$		$RCH{=}CAm{\cdot}CH_2OH$ (28) New	$RCH_2CHAm{\cdot}CH_2OH$ (15) New	$RCH_2CHAm{\cdot}CH_3$ (21) New
p-$CH_3C_6H_4$—	$RCH{=}CMe{\cdot}CHO$ (7) New		$RCH{=}CMe{\cdot}CH_2OH$ (29) New		
	$RCH{=}CEt{\cdot}CHO$ (8) New				
o-$CH_3OC_6H_4$—	$RCH{=}CMe{\cdot}CHO$ (5) New	$RCH_2CHMe{\cdot}CHO$ (12) New		$RCH_2CHMe{\cdot}CH_2OH$ (19) New	$RCH_2CHMe{\cdot}CH_3$ (25) New
	$RCH{=}CEt{\cdot}CHO$ (6) New	$RCH_2CHEt{\cdot}CHO$ (13) New		$RCH_2CHEt{\cdot}CH_2OH$ (20) New	$RCH_2CHEt{\cdot}CH_3$ (26) New
p-$CH_3OC_6H_4$—	$RCH{=}CMe{\cdot}CHO$ (4) New				
	$RCH{=}CEt{\cdot}CHO$	$RCH_2CHEt{\cdot}CHO$ (11) New		$RCH_2CHEt{\cdot}CH_2OH$ (18) New	$RCH_2CHEt{\cdot}CH_3$ (24) New
$CH_2{<}^{O}_{O}{>}C_6H_3$— (3, 4)	$RCH{=}CH{\cdot}CHO$		$RCH{=}CH{\cdot}CH_2OH$ (30) New	$RCH_2CH_2CH_2OH$ (14) New	$RCH_2CH_2CH_3$ (21a)
	$RCH{=}CMe{\cdot}CHO$ (1) New		(13a)	$RCH_2CHMe{\cdot}CH_2OH$ (16) New	$RCH_2CHMe{\cdot}CH_3$ (22) New
	$RCH{=}CEt{\cdot}CHO$ (2) New	$RCH_2CHEt{\cdot}CHO$ (10) New		$RCH_2CHEt{\cdot}CH_2OH$ (17) New	$RCH_2CHEt{\cdot}CH_3$ (23) New
	$RCH{=}CAm{\cdot}CHO$ (3) New				

The figures are preparation numbers in the text.

The unsaturated aldehydes were prepared by the usual method of condensation in alkaline solution, a method almost uniformly successful [20] though the yields are usually low. Efforts at improvement of the technique of such condensations, aiming at yield from aromatic aldehyde, resulted in the use of weakly alkaline solutions, aqueous alcoholic, over a long time, and is exemplified in the preparation of alpha-methyl 3-4 methylene dioxy cinnamic aldehyde. However, a less tedious method, aiming at yield from aliphatic aldehyde, appeared in publication in the course of the work, a method involving the use of strongly alkaline alcoholic solutions.[45] It represented a better technique in that the yields were better, the time constant, and the unused aromatic aldehyde was recoverable if desired, and it was used in later preparations, exemplified in the case of alpha-ethyl 4-methyl cinnamic aldehyde. The aldehydes were found to be either faintly yellow liquids or almost colorless (one was colorless) solids. Their boiling points lay close to those of the corresponding saturated alcohols and their melting points showed no regularity. In bisulphite formation a regularity appeared in using a standard method of formation, a regularity that found application as a means of separation of some of these aldehydes from the aldehydes they were derived from, or from the saturated aldehydes formed during catalytic reduction. The alpha-methyl unsaturated aldehydes all formed bisulphite compounds in less than a day when shaken in 30% to 50% ether solution with 4 to 7 volumes of a solution of saturated sodium bisulphite, whereas the alpha-ethyl (or higher) derivatives formed none over many weeks, no matter how the benzene nucleus was substituted. Concerning the formation of bisulphite compounds in the acroleins generally[17, 6, 14, 2] there seems to be no regularity, and the present instance is valid only in the circumstances outlined, since it is possible, for instance, to get a bisulphite compound from alpha-ethyl cinnamic aldehyde if no solvent is used. The aldehydes react in the ordinary way with hydroxylamine and phenylhydrazine, the sodium salts of the oximes being probably easily hydrolyzed and the oximes are distillable. Cases of

condensation with acetone, through alkali, were observed and some of the phenylhydrazones were tried, at hazard, for rearrangement to pyrazoline, all of them giving positive tests for the rearrangement.[10] They reduce ammoniacal silver nitrate on boiling, usually without formation of a mirror in the ordinary circumstances, in contradistinction to the saturated aldehydes derived from them which all give mirrors on warming or boiling. They decolorize bromine in carbon tetrachloride at room temperatures without evidence of hydrobromic acid, but not instantly, the color appearing through the extent of the solution to disappear in times from seconds to minutes. This test with the unsaturated alcohols, on the contrary, gave no trace of color in the extent of the solution until near the saturation point, a result in line with known results on the effect of the negativity of groups in such positions on the rate of bromine absorption.[26]

The unsaturated alcohols were prepared by the method of reduction with metal alcoholate from the unsaturated aldehydes[33, 43] a reaction[38, 44] recently applied with some success as a preparative method, using aluminum or other ethylates, for alcohols from aldehydes. They were colorless liquids (one a colorless solid) giving urethanes, and their boiling points were the highest of all the classes (from 17° C. to 4° C. above the unsaturated aldehydes at about 5mms.), and differ from the other classes also in their behavior to bromine (see unsaturated aldehydes). No representatives of this group are otherwise known, and the alpha-unsubstituted representative "cubebin" which is important in its relation to natural "cubebin," is here described for the first time. Natural "cubebin" was for long understood to be the alcohol described here (3-4 methylene dioxy cinnamic alcohol), and the monomolecular form has been sought and claimed by Pauly et al.[37] by reduction of 3-4 methylene dioxy cinnamic aldehyde with iron and acetic acid. A pseudo-cubebin has also been described by Haberkann[24] and it is curious that all of them melt near 120° C., though only one of them (Pauly) has been distilled. This one is described with a rough boiling point (higher than here observed) and melting at 123° C. No derivatives were described though the phenyl urethane of cinnamic alcohol was described in the same paper for the first time. Its behavior with

formic acid was comparable to that of cinnamic alcohol and it decolorized permanganate solution. The high melting point compared with the corresponding unsaturated aldehyde might alone be suspicious if it were not for the fact that cinnamic alcohol is abnormal in this respect, and that coniferyl alcohol (the last of a trio of such alcohols known) has been little studied.[1, 29, 30] The alcohol has been here prepared by a method tested by the author, as the fourth in sequence of always successful results, is described in terms of boiling point, melting point, benzoate, phenyl urethane, permanganate solution, bromine solution, and catalytic reduction leading to the unmistakable odor of the safrole type, all in agreement with results on the other unsaturated alcohols prepared. **The saturated aldehydes** were isolated from their bisulphite compounds (see on) and are all colorless mobile liquids with boiling points lower than the corresponding saturated alcohols or unsaturated aldehydes. **The saturated alcohols** are all colorless viscous liquids, prepared from the middle fractions of the reduction products of the unsaturated aldehydes after oximation to remove aldehydes. In one case the best method of isolation was via the acetate by distillation or alternatively via the dinitro-benzoate by virtue of its low solubility in alcohol.

The propanes $-CH_2CHR{\cdot}CH_3$. These were found in the first fractions of the distillates of the reduction products of the unsaturated aldehyde $-CH=CR{\cdot}CHO$. If necessary, they were purified by oximation to remove aldehydes and were all colorless, very mobile, liquids, all odoriferous, giving no evidence of admixture with propenes.

The hydrogenation of the unsaturated aldehydes. The reductions were carried out by the method of Skita,[23] a method usually leading only to hydrogenation of the $-CH=CH{\cdot}CHO$ group in parallel circumstances to those used here, with no attack of the benzene nucleus or formation of bimolecular compounds. However, Skita has reported the formation of a bimolecular compound from citral in circumstances much the same as these,[19] citral having two ethylenic bonds, and a bimolecular compound

$PhCH_2CH_2CH(OH)CH_2CH_2CH_2Ph$ has been isolated by Braun and Kochendorper[32] from cinnamic aldehyde by hydrogenation with nickel at high temperatures. A bimolecular aldehyde has been reported from an acrolein by electrolytic reduction (Hibbert and Read [36]), condensation of the aldol type leading to ring formation at the same time. In the hydrogenation of cinnamic aldehyde with platinum oxide-black Adams and Tuley[38] have described a preferential reduction either to saturated aldehyde or unsaturated alcohol by suitable poisoning of the catalyst. The conditions, however, were of a highly specific nature, needing prolonged experimentation for each case to find the proper proportions of mixed poisons. Skita[23] obtained by reduction of cinnamic aldehyde, using one mole of hydrogen, almost pure saturated aldehyde (hydrocinnamic aldehyde) but this result could not be duplicated by Straus and Grindel [35] who obtained in the same circumstances only a little of the saturated aldehyde, some saturated alcohol, and propane. In general, indeed, these later investigators found with cinnamic aldehyde the general production of saturated alcohol, propane, a little unsaturated alcohol, and no saturated aldehyde. Taking the one case of isolation of saturated aldehyde to be inexplicably abnormal, since in all other cases with variation of conditions (particularly pressure and proportion of hydrogen and catalyst) they obtained the products just mentioned, they postulated the reduction of the unsaturated aldehyde to be according to the scheme:

$$\begin{array}{l} -CH{=}CH\cdot CHO \rightarrow (-CH{=}CH\cdot CH_2OH) \rightarrow (-CH{=}CH\cdot CH_3) \\ \qquad\qquad\qquad\qquad\quad \downarrow \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad -CH_2CH_2CH_2OH \qquad -CH_2CH_2CH_3 \end{array}$$

In support they quoted a parallel easy reduction of an ether of an unsaturated alcohol of the same type[22] and the fact that they found no reduction of the saturated aldehyde (dihydrocinnamic aldehyde) in the same circumstances. Since the saturated alcohol is also not reduced in the same circumstances, the scheme explains the products, the ones in parentheses being isolated in small quantities or not at all by virtue of their faster reduction than the unsaturated aldehyde simultaneously undergoing reduction. Thus a course of reaction is assumed which does not in-

volve the saturated aldehyde or saturated alcohol, these being not postulated as intermediates because of the fact of non-reducibility, the underlying assumption being that any product found non-reducible after isolation from the reaction mixture must be assumed non-reducible in the course of the reaction wherever postulated. However, in order to maintain the validity of that argument a special property of the unsaturated aldehyde has been assumed, namely that the aldehyde group is reduced to the exclusion of the double bond, the same special property being given, to a lesser extent, to the unsaturated alcohol since this is attacked at the double bond and the alcohol group. The argument could be maintained in the case of the unsaturated aldehyde, without ascribing any special ease of reduction to the aldehyde group, by assuming 1-4 addition to a vinyl alcohol with subsequent rearrangement to saturated aldehyde and reduction to saturated alcohol simultaneously. However, such argument could not explain the production of a propane from the unsaturated alcohol. Now the general behavior of this catalyst is the hydrogenation of the double bond and not the aldehyde, alcohol or ketone groups, as evidenced in the history of its use in the past. In this work, also, it is found that the production of the saturated aldehyde is the normal course of the reaction, that the unsaturated alcohols are not isolated, and that ethylenic substances are not isolated. Since this is the result for a whole series of such aldehydes, it argues strongly against ascribing any special ease of reduction to the aldehyde group in the unsaturated aldehydes, and against any special non-reduction of the double bond in those aldehydes. It is true that the unsaturated alcohols tested herein were very easily reduced, and, as claimed by the authors, the saturated aldehyde is not reducible in these circumstances. But, as far as the actual isolations are concerned, there was no evidence of any ethylenic substances at all, and the postulated course of the reaction must be left aside as not proved. As a synthetic method it could be used for non-ethylenic substances, these being isolated in each case, though in one instance the saturated aldehyde was not isolated, but became evident on change of solvent. The saturated alcohol and saturated aldehyde were the major products with a one mole or

two mole hydrogenation, the propane being present only in small quantities in each case. The limit of hydrogenation, with repeated use of catalyst, was near two moles of hydrogen and some of the unsaturated aldehydes absorbed proportionately more hydrogen to catalyst than others. The catalyst was found to be not poisoned with addition of traces of iron, cobalt, nickel salts and in this respect must be compared to platinum. The catalyst contained traces of platinum, rhodium, and hydrochloric acid, probably a fair specimen of "pure" palladous chloride from normal sources. In the examination of the course of the reduction the production of residues on distillation of the reduction products was often a complicating factor, and they were examined to dispose of the possibility of formation of bimolecular compounds, or reaction involving some products not isolated (unsaturated alcohols reacting). The experiments are detailed in Section B, leading to the conclusion that the residues are due to pyrolysis involving the saturated alcohol, probably giving ethers, not involving any unsaturated alcohol, are probably the result of traces of impurities (sulphuric acid through oxidation in the bisulphite compounds, etc.) and reducible to smaller and smaller proportions by change of technique.

Odor. Among the unsaturated aldehydes only the derivatives of cinnamic aldehyde proper (i. e., without ring substitution) were markedly odoriferous. Homologous substitution at the double bond shows a great difference as between the lower members and the alpha-amyl substituted cinnamic aldehyde. In the unsaturated alcohols such a change is not evident, and even the ring-substituted unsaturated alcohols prepared gave no evidence of being changed in odor type, all of them that were odoriferous being of the soft floral type of cinnamic alcohol itself. The saturated alcohols were not markedly odoriferous and so cannot be compared. The saturated aldehydes showed no great change on substitution at the same position as the corresponding unsaturated aldehydes (the alpha-position to the aldehyde) and the same was true of the propanes, though both groups showed change of odor type with changing ring substitution. Thus all the substituted dihydro-safroles were strongly reminiscent of the

well known safrole, and substituted dihydroanetholes of anethole. Only the unsaturated aldehydes, therefore, showed marked change with homologous change at that position, and they are in that respect abnormal, at least as far as the examples show. The variety and type explanation would perhaps not be amiss in this case,[25, 31] treating the unsaturated aldehyde as derivatives of aliphatic aldehydes, since the aldehydes of the aliphatic series show changes of odor type near the C_6 mark, a change not notable with the alcohols. However, this has not been checked with the saturated aldehydes, alpha-substituted with higher groups, in this work.

An introductory study has been made in the series of alpha-substituted cinnamic aldehydes and the related unsaturated alcohols, saturated alcohols, saturated aldehydes and propanes, and some thirty such compounds have been prepared. The method of Skita for catalytic reduction of these aldehydes (unsaturated) has been shown to be applicable for the production of non-ethylenic substances only, establishing a fair presumption for the behavior of such unsaturated aldehydes generally and supplementing the meagre and insecure reports for cinnamic aldehyde itself. These unsaturated aldehydes have been shown to be convertible to the unsaturated alcohols by a method now brought into clear relief as a valuable method for change of unsaturated aldehyde to unsaturated alcohol, with the important practical result of non-admixture with original aldehyde, an example of its value being adduced in the preparation of an important monomolecular "cubebin" which has not been obtained, though sought, and once claimed, by older methods involving reduction with iron and acetic acid. These unsaturated aldehydes have been examined comparatively to ascertain the effect of homologous change at the double bond on odor, with the conclusion that the change is abnormal, at least as far as ordinary laboratory tests are valid in that field.

EXPERIMENTAL (Section A)

Prep. (1) Alpha-methyl 3-4 methylene dioxy cinnamic aldehyde. This was prepared by condensation in alkaline solution, aqueous alcoholic, using heat and little alkali. As between this method and the second method already referred to a direct comparison of yields is given in preparation (2) of this section. In this preparation 40 gms. of piperonal (heliotropin, 3-4 methylene dioxy benzaldehyde) were dissolved in a mixture of 400 cc. of alcohol and 1800 cc. of water, the temperature being kept at 65°-70° C. for 73 hours while two moles of propaldehyde (about 36 cc.) were added, 23 cc. at the beginning of the experiment and the remainder uniformly in 3 cc. portions for the next 60 hours, the mixture kept alkaline to litmus by the addition of aqueous (10% solution) sodium hydroxide as required by test, one cc. at a time, and 2 cc. when leaving overnight. During the day the mixture was stirred continuously with a mechanical stirrer. After cooling the mixture was made acid with acetic acid, extracted with benzene, the solution dried and the solvent removed. Very little piperonal remained (distilling from 100° to 130° C. (4 mm.) and the distillate from 140° C. to 160° C. (4 mm.) set solid. This was crystallized from petroleum ether, yield 15 gms., light cream crystals, M. P. 65½°-66½° C. (uncorr.)

Analysis: Calculated for $C_{11}H_{10}O_3$ C = 69.44% H = 5.30%
Found: C = 69.43% H = 5.25%

The phenyl hydrazone, yellow crystals from absolute alcohol, by reaction of phenylhydrazine hydrochloride (1 mol.) with the aldehyde (1 mol.) and sodium acetate (2 mol.) in dilute alcohol on the water bath for one hour, M. P. 121°-123° C. (uncorr.). The oxime, from dilute alcohol solution by warming with 1.2 moles hydroxylamine in aqueous alcohol on the water bath for one hour, colorless crystals M. P. 124°-125° C. (uncorr.). The aldehyde itself has a very faint odor. The phenylhydrazone, dissolved in acetic acid with or without the addition of a little concentrated sulphuric acid, gave no color reaction with a solution of sodium nitrite, ferric chloride, or potassium dichromate. After the acetic acid solution had been refluxed for ten minutes or more and cooled, a drop of concentrated sulphuric acid added, a posi-

tive color test was given with all the mentioned reagents for pyrazoline.[10] The aldehyde decolorized bromine in carbon tetrachloride and gave a bisulphite compound under the conditions given ahead.

Prep. (2) Alpha-ethyl 3-4 methylene dioxy cinnamic aldehyde. As in preparation (1), 20 gms. of piperonal in a mixture of 400 cc. of 95% alcohol and 1800 cc. of water at 60° C., using two moles of butyl aldehyde in 50 hours of heating, gave only 25% of the cinnamic aldehyde. For comparison the later method gave a 50% yield, using only one mole of butyraldehyde, calculating from the piperonal in both cases. In the separation of the aldehyde by distillation in nitrogen (all distillations were done in nitrogen) the second fraction around 160° C. to 170° C. (5 mm.) was redistilled. This distillate solidified and was crystallized from petro-ether (with a little benzene or not) in light pale yellow crystals M. P. 56°-57° C. (uncorr.)

Analysis: Calculated for $C_{12}H_{12}O_3$ C = 70.5% H = 5.9%
Found: C = 69.95% H = 5.79%

The phenylhydrazone, from 60% alcohol in water, in long pale yellow needles M. P. 118°-120° C. (uncorr.)

Analysis: Calculated for $C_{18}H_{18}O_2N$ C = 73.43% H = 6.17%
Found: C = 72.77% H = 6.08%

The oxime, white, from 60% alcohol M. P. 141°-143° C. (uncorr.)

The aldehyde was odorless, decolorized bromine solutions in a few seconds, and gave no bisulphite compound (see above).

Prep. (3) Alpha-amyl 3-4 methylenedioxy cinnamic aldehyde. 75 gms. of piperonal were added to a solution of 5 gms. of potassium hydroxide in 125 gms. of 95% alcohol. With continuous stirring at about 10° C., 50 gms. of heptaldehyde were added, drop by drop, in the course of 4½ hours and the mixture allowed to stand ½ hour. Excess of acetic acid was then added and the mixture thrown into a large excess of water, the whole being extracted with benzene, the extract washed with a little sodium carbonate solution and water. The solvent was removed

after drying. The residue distilled (in nitrogen as always) at 3mm. pressure gave a fraction at 170°-180° C. which was redistilled and collected near 170° C. (3 mm.), the yield being 30 gms. of a viscous yellow liquid not solidifying in a freezing mixture. B. P. 165°-167° C. (3 mm. uncorr.) for analysis.

Analysis: Calculated for $C_{15}H_{18}O_3$ C = 73.13% H = 7.37%
Found: C = 72.90% H = 7.32%

Practically odorless, giving $n_D^{23} = 1.58587$ and a phenylhydrazone, yellow, M. P. 85°-87° C. (uncorr.) which gave a positive test for rearrangement to pyrazoline as before and no bisulphite compound (see above).

Prep. (4) Alpha-methyl 4-methoxy cinnamic aldehyde. By the first method, the time requiring prolongation to 120 hours for fair yield. 45 gms. of anisaldehyde (4-methoxy benzaldehyde) and two moles of propaldehyde gave thus a yield of 20 gms. at 160°-165° C., nearly pure, at 9 mm. pressure. For analysis B. P. 172°-174° C. (15 mm.. uncorr.), a light yellow oil which gave a bisulphite compound as before.

Analysis: Calculated for $C_{11}H_{12}O_2$ C = 74.96% H = 6.87%
Found: C = 74.24% H = 7.01%

The phenyl hydrazone gave a positive test for rearrangement to pyrazoline, and the oxime, pure white, crystallizes from aqueous alcohol. A portion of the aldehyde was condensed with acetone by means of sodium hydroxide and gave two crystalline products, probably the mono and di-alkylidene acetones. The same reaction went easily with alpha-ethyl cinnamic aldehyde, using a slight excess of acetone in 2% alcoholic potassium hydroxide and warming for ten minutes on the water bath, followed by precipitation with water as a yellow solid easily crystallized from alcohol and analyzing thus:

Calculated for $C_{14}H_{16}O$ C = 83.9% H = 8.05%
Calculated for $C_{25}H_{26}O$ C = 87.7% H = 7.66%
Found: C = 87.8% H = 7.76%

and it is thus the di-alkylidene acetone M. P. 104°-105° C. (corr.) PhCH = CEtCH = CHCOCH = CHCEt = CHPh.

Prep. (5) Alpha methyl 2-methoxy cinnamic aldehyde. 150 gms. of 2-methoxy benzaldehyde were added to a solution of 10 gms. of potassium hydroxide in 240 gms. of 97.5% alcohol, and in the course of 6½ hours at about 5° C., 60 gms. of propaldehyde were added drop by drop with stirring. The mixture was allowed to stand for ½ hour, the temperature rising to 15° C. in that time. As before, the distillate from 133°-145° C. (5¾ mm.) being collected. Yield 80 gms. For analysis at B. P. 128° C. (4¼ mm., corr.). There was very little residue. It gave a bisulphite compound. It is a light yellow oil of a slight deep odor resembling more o-methoxy benzaldehyde than the cinnamic aldehydes.

Analysis: Calculated for $C_{11}H_{12}O_2$ C = 74.96% H = 6.87%
Found: C = 75.05% H = 7.03%

Prep. (6) Alpha-ethyl 2-methoxy cinnamic aldehyde. 250 gms. of 2-methoxy benzaldehyde were added to a solution of 16.6 gms. of potassium hydroxide in 500 cc. of 99% alcohol and, with stirring, 120 cc. of butaldehyde added drop by drop in the course of 6½ hours at about 5°C., the temperature rising in the last two hours to 20° C. The mixture was allowed to stand ¼ hour. The product, as in the preceding examples, was collected at 125°-140° C. (4½ mm.). Redistilled and collected at 131°-133° C. (4½ mm.) the aldehyde solidified to pure white crystalline mass of M. P. 48¼°-48¾° C. (uncorr.) and distilled at 140°-141° C. (5½ mm.) (corr..). It can be recrystallized from alcohol. It gave no bisulphite compound (see ahead). Odorless.

Analysis: Calculated for $C_{12}H_{14}O_2$ C = 75.74% H = 7.42%
Found: C = 75.5% H = 7.59%

Prep. (7) Alpha-methyl 4methyl cinnamic aldehyde. 82 gms. of p-tolualdehyde were added to 6 gms. of potassium hydroxide dissolved in 180 cc. of absolute alcohol and 39 cc. of propaldehyde were added in the course of 4½ hours near 0° C., the mixture being allowed to stand for ¼ hour without further cooling, stirring and addition in the same way as before. Col-

lected as before, the product was isolated at 128½°-130½° C. (11 mm.) (corr.).

Analysis: Calculated for $C_{11}H_{12}O$ C = 82.45% H = 7.56%
Found: C = 82.22% H = 7.49%

It was a light yellow liquid, solidifying to a low melting solid, with a faint heavy odor like p-tolualdehyde and pervasive. It gave a bisulphite compound, yield being 45 gms.

Prep. (8) Alpha-methyl 4-methyl cinnamic aldehyde. 115 gms. of p-tolualdehyde were added to a solution of 9 gms. of potassium hydroxide in 270 cc. of 95% alcohol and to the solution were added in the course of 4 hours at about 18° C. some 50 cc. of butaldehyde, drop by drop, with constant stirring. As before, collected at 130°-144° C. (11 mm.) and for analysis at 137½° C. (11½ mm.), a light yellow oil solidifying to a low melting solid, yield 80 gms.

Analysis: Calculated for $C_{12}H_{14}O$ C = 82.71% H = 8.09%
Found: C = 82.62% H = 8.22%

Decolorizes bromine solutions in a few seconds, and dilute permanganate solutions, the odor being vague and sweet, resembling alpha-ethyl cinnamic aldehyde.

Reduction of 3-4-methylene dioxy cinnamic aldehyde. Tests were carried out with this on the platinum oxide-black method of reduction of Adams and Tuley[26] and it was found necessary to resort to re-activation three times to obtain the two mole hydrogenation effected with palladium below. There was evidence of the same resultants as below, and indications that a search for an ameliorant of a specific reduction to unsaturated alcohol or saturated aldehyde, as found by them with cinnamic aldehyde would be a long, doubtful process for each aldehyde chosen. By the method of Skita, 12 gms. of the aldehyde, dissolved in 125 cc. of 95% alcohol and 40 cc. of water, were mixed with 20 cc. of 2% gum arabic solution in water and 10 cc. of 1% palladous chloride solution in water and brought immediately to hydrogenation in an Adams hydrogenator at 3 atmos. pressure. After 45 minutes the absorption of hydrogen (electrolytic commercial

hydrogen direct) ceased abruptly and two moles of hydrogen were found to have been absorbed (the pressure being then 2 atmos., making an average pressure of 2½ atmos.). The catalyst was filtered off from the colorless product and the filtrate thrown into excess of water and extracted with ether, the ether solution being then treated with 4-6 volumes of saturated sodium bisulphite for a day with occasional good shaking. The ether solution itself contained about 15-25% of the reduction product and these were the conditions employed for the formation of bisulphite compound from aldehyde in all the later reductions, varying only the time of contact with sodium bisulphite solution to greater length as seemed desirable. The bisulphite compound thus thrown out was filtered off and washed well with ether, the washings being added to the filtrate. The ether layer of the filtrate was run off and washed well with a solution of sodium carbonate and water finally. The ether solution was then dried and the solvent distilled off and the residue then distilled. The first portions of the distillate (all distillations were done in nitrogen at reduced pressure) were found to give the propane (dihydrosafrole) without admixture with any propene. Tested for isosafrole, which boils close to dihydrosafrole, there was found to be no rearrangement with potassium hydroxide in conditions which should lead to a higher boiling safrole. The odor of this dihydrosafrole is found to be the same as safrole and powerful, not, as described elsewhere, fainter than safrole.

Analysis: Calculated for **dihydrosafrole** $C_{10}H_{12}O_2$

$C = 73.13\%$ $H = 7.37\%$

Prep. 21a Found: $C = 73.41\%$ $H = 7.55\%$

Calculated for isosafrole, or safrole

$C = 74.04\%$ $H = 6.22\%$

The remainder, distilling near 150° C. (6 mm.) was found to give the saturated alcohol (**3-4 methylene dioxy dihydrocinnamic alcohol, Prep. No. 14)** as a colorless viscous liquid of B. P. 149°-150° C. (6 mm., uncorr.), odorless.

Analysis: Calculated for $C_{10}H_{12}O_3$

$C = 66.64\%$ $H = 6.72\%$

Found: $C = 66.63\%$ $H = 6.69\%$ $n_D^{21} = 1.54427$

There was found to be no residue from the distillation. The **acetate** of the alcohol, by treatment with excess of acetic anhydride and sodium acetate for two hours, was found to distill at 145° C. (4mm., uncorr.), having a slight odor of the ester type.

Analysis: Calculated for $C_{12}H_{14}O_4$ C = 64.83% H = 6.35%
Found: C = 64.92% H = 6.58%

Reduction of alpha-methyl 3-4 methylenedioxy cinnamic aldehyde. As above, 5 gms. of the aldehyde, 150cc. of 95% alcohol, 5cc. of the catalyst solution, 20 cc. of the gum arabic solution, 30 cc. of water, mixed, absorbed two moles of hydrogen in 40 minutes with no excess pressure, absorption ceasing abruptly. From a series of reductions with such proportions, except in the aldehyde where 10 gms. were used instead of 5 gms., stopping the reduction at 1¼ moles of hydrogen for all three reduction products to be obtained, treated as in the preceding example, the bisulphite compound obtained was decomposed by shaking with sodium carbonate solution and ether until the solid disappeared and then washing the ether solution with water, drying, driving off the solvent. The residue was found to be almost pure unchanged aldehyde and not, as in other cases, the saturated aldehyde. From a similar reduction performed in acetic acid solution, however, a mixture of the unchanged aldehyde and the expected aldehyde was obtained, boiling from 140° C. to 158° C. (4½ mm., uncorr.), the saturated aldehyde being the lower boiling, having a sharp odor, a liquid, giving a mirror with ammoniacal silver nitrate. After the removal of the bisulphite compound from the reduction products of the aqueous-alcoholic reduction just described the residual ether solution was separated from the aqueous layer of saturated sodium bisulphite solution and washed as before with sodium carbonate solution and finally water. The solvent being removed, the residue gave two portions on distillation, one near 120° C. (4 mm.), the other near 150° C. (4 mm.). The first portion, redistilled, gave the propane **(Prep. No. 22) 2-methyl 3(3-4 methylenedioxy phenyl) propane,**

a colorless, mobile oil with a strong safrole odor, B. P. 238°-240° C. (uncorr., 760 mm.).

Analysis: Calculated for $C_{11}H_{14}O_2$

$C = 74.13\%$ $H = 7.85\%$

Found: $C = 73.99\%$ $H = 7.815\%$ $n_D^{23} = 1.51841$

The higher portion gave the saturated alcohol **(Prep. No. 16) alpha-methyl 3-4 methylenedioxy dihydrocinnamic alcohol,** after treating with hydroxylamine to remove aldehydes as higher boiling oximes which remained behind as crystalline residues, the alcohol distilling at 147°-148° C. (4 mm., uncorr.) as a viscous odorless liquid, stable to solutions of bromine in carbon tetrachloride.

Analysis: Calculated for $C_{11}H_{14}O_3$

$C = 68.0\%$ $H = 7.27\%$

Prep. No. 16 Found $C = 68.08\%$ $H = 7.41\%$

Found: $C = 67.97\%$ $H = 7.40\%$ $n_D^{22\frac{1}{2}} = 1.54054$

No residues were obtained on distillation, and no trace of unsaturated alcohol was found in the saturated alcohol or the oximes.

Reduction of alpha-ethyl 3-4 methylenedioxy cinnamic aldehyde. 10.2 gms. of the aldehyde dissolved in 100 cc. of 95% alcohol with the addition of 20 cc. of water, 10 cc. of the gum solution and 5 cc. of the catalyst successively, absorbed 1.8 moles of hydrogen in 90 minutes, using no excess pressure. 10.2 gms. of the aldehyde in 65 cc. of glacial acetic acid, 30 cc. of water, 7 cc. of gum solution, and 5 cc. of catalyst solution, absorbed 1.6 moles of hydrogen in two hours. In this instance, from the reduction in aqueous-alcohol, the isolated bisulphite compound (see above for conditions) was decomposed as before and gave an aldehyde distilling at 136° C. (3 mm., uncorr.) **(Prep. No. 10)** which was not contaminated with unchanged aldehyde and required no purification, being **alpha-ethyl 3-4 methylenedioxy dihydrocinnamic aldehyde.** It was a liquid, colorless, having an odor slighter and sweeter, but resembling,

alpha-ethyl dihydrocinnamic aldehyde in the sharp quality of the odor.

Analysis: Calculated for $C_{12}H_{14}O_3$ C = 69.86% H = 6.85%
Found **(Prep. No. 10)** C = 70.21% H = 6.82%

The ether residues, treated as before, gave a portion below 130° C. (3 mm.) which was the propane, collected at 255°-260° C. (760 mm., uncorr.), most at 257° C., a slightly impure specimen, having the same strong safrole odor as dihydrosafrole.

Analysis **(Prep. No. 23) 2-ethyl 3(3-4 methylenedioxy phenyl) propane,** a mobile colorless oil:

Calculated for $C_{12}H_{16}O_2$ C = 74.95% H = 8.39%
Found: C = 73.93% H = 8.28%

In the distillates above the propane the main fraction near 150° C. (2mm.) was collected and oximated as if it were all aldehyde, the excess hydroxylamine removed with acid and finally the product washed with sodium carbonate solution and water. In all cases this oximation process was done in aqueous alcohol on the water bath for one hour, the product thrown into excess water, extracted with ether, and the ether extract treated with hydrochloric acid to remove any excess hydroxylamine, washed well with water, then the carbonate solution, and finally water. The saturated alcohol was obtained **(Prep. No. 17), alpha-ethyl 3-4 methylenedioxy dihydrocinnamic alcohol,** requiring repeated distillation to remove a residual crystalline oxime, and boiling at 148°-150° C. (2 mm., uncorr.). It is a viscous, colorless, liquid, odorless. $n_D^{22} = 1.53853$.

Analysis: Calculated for $C_{12}H_{16}O_3$ C = 69.19% H = 7.75%
Found: C = 68.89% H = 7.57%

In the distillation of the reduction products in this instance a residue was observed which behaved like the residues discussed in the appendix B.

Reduction of alpha-ethyl cinnamic aldehyde. With proportions of the aldehyde and catalyst as in the first case of reduction given the aldehyde absorbs less hydrogen, and more slowly.

Aldehyde 23 gms., alcohol 95% 110 cc., water 30 cc., gum solution 10 cc., catalyst solution 10 cc., absorbed less than one mole of hydrogen in 45 minutes. 10 cc. more catalyst solution being added, the absorption reached a total of 1¼ moles of hydrogen, being then very slow. The reduction was then stopped, no excess pressure being used. The bisulphite compound, as before, was decomposed and gave the pure saturated aldehyde **(Prep. No. 9) alpha-ethyl dihydrocinnamic aldehyde,** as a colorless liquid, giving a mirror with ammoniacal silver nitrate, having a sharp odor with a resemblance to menthol in penetration, pleasant, with B. P. 115°-116° C. (12½ mm., uncorr.). It was not reducible by the method of Skita in the same circumstances as the unsaturated aldehyde but absorbed hydrogen using platinum oxide-black under pressure.

Analysis: Calculated for $C_{11}H_{14}O$
C = 81.42% H = 8.70%
Found **(Prep. No. 9)**
C = 81.39% H = 9.26% $n_D^{22\frac{1}{2}} = 1.50839$

From the residual ether solution the propane was found in the first portions of the distillate after removal of solvent **(Prep. No. 20a).** The first portions were oximated as given in the preceding page and the propane, **2-ethyl 3-phenyl propane,** was found of B. P. 190° C. (710 mm., uncorr.) being given previously as of B. P. 192° C. (715 mm., no mention of corr.)[44] This propane, as well as alpha-amyl 3-phenyl propane described further on, gave trouble in analysis, both being hydrocarbons extracted with ether, and possibly impure with ether not removable.

Analysis: Calculated for $C_{11}H_{16}$ C = 89.11% H = 10.38%
Found: C = 87.13% H = 10.38%

The odor of this propane was sweet, somewhat resembling safrole. In the higher portions of the distillate, after oximation as described on page 23, the saturated alcohol was found, **alpha-ethyl dihydrocinnamic alcohol (Prep. No. 14a)** as a colorless, viscous liquid with a faint, dull sweet odor hard to characterize. It has been previously described as rose-like. B. P. 105°-107° C.

(4 mm., uncorr.) and 249°-250° C. (735 mm., uncorr., corr. being about 7° C. at this temp.). Previous preparation.[17]

Analysis: Calculated for $C_{11}H_{16}O$ C = 80.43% H = 9.83%
Found **(Prep. No. 14a)** C = 80.19% H = 9.63%

The residue after removing these individuals from the reduction products is described in detail in section B.

Reduction of alpha-ethyl 4-methoxy cinnamic aldehyde. 14 gms. of the aldehyde, 100 cc. of 95% alcohol for solution, then 30 cc. of water and 10 cc. of gum solution followed by 10 cc. of catalyst, as before, hydrogenated at an average pressure of 2 atmos., absorbed circa two moles of hydrogen with evolution of heat. A little more hydrogen is absorbed with higher proportion of catalyst. The bisulphite compound, as before, gave the pure saturated aldehyde **alpha-ethyl 4-methoxy dihydrocinnamic aldehyde (Prep. No. 11)** as a colorless liquid B. P. 116°-117° C. (3 mm., uncorr.), giving a mirror with ammoniacal silver nitrate, resembling in odor the saturated aldehyde just discussed in the preceding reduction but not so sharp in odor.

Analysis: Calculated for $C_{12}H_{16}O_2$
C = 74.95% H = 8.39%
Found: C = 74.61% H = 8.55%

The residual ether solution, as before, gave a lower fraction near 105°-110° C. (10 mm.) which was oximated to remove aldehydes (see above) and the propane isolated from the resultant at B. P. 135°-136° C. (29 mm., uncorr.), having a strong anethole odor, colorless, mobile.

Analysis: **2-ethyl 3(4-methoxy phenyl) propane**
Calculated for $C_{12}H_{18}O$ C = 80.83% H = 10.19%
Found **(Prep. No. 24)** C = 80.15% H = 9.92%

The next fraction in the distillation, near 140° C. (3 mm.) was oximated and gave the saturated alcohol, **alpha-ethyl 4-**

methoxy dihydrocinnamic alcohol, as a viscous, colorless, odorless liquid, with B. P. 129°-130° C. (2½ mm., uncorr.).

Analysis: Calculated for $C_{12}H_{18}O_2$
$C = 74.17\%$ $H = 9.35\%$
Found **(Prep. No. 18)**
$C = 74.42\%$ $H = 9.64\%$ $n_D^{22} = 1.52398$

In this distillation, from 36 gms. of reduction product absorbing 1.6 moles of hydrogen 4 gms. of the saturated aldehyde were obtained, 4 gms. of the propane fraction, 4 gms. intermediate between propane and saturated alcohol, 10 gms. of saturated alcohol, and 10 gms. of a residue not in the monomolecular class. This residue is thus approximately that of a product absorbing two moles of hydrogen if homogeneous, the proportion of hydrogen in all cases in the residues being near this, but analyzing as if dehydrated (see section B).

Reduction of alpha-methyl 2-methoxy cinnamic aldehyde. As before, aldehyde 21 gms. alcohol 150 cc. of 95%, water 30 cc., gum solution 10 cc., catalyst 12 cc. At an average pressure of 2½ atmos. the mixture absorbed 1.9 moles of hydrogen in 60 minutes with evolution of heat. The bisulphite compound, isolated as on page 21, gave the pure saturated aldehyde **alpha-methyl 2-methoxy dihydrocinnamic aldehyde (Prep. No. 12)** as a liquid with a dull sweet odor, giving a mirror with ammoniacal silver nitrate, of B. P. 113°-114° C. (5¼ mm. uncorr.).

Analysis: Calculated for $C_{11}H_{14}O_2$ $C = 74.11\%$ $H = 7.93\%$
Found: $C = 74.11\%$ $H = 8.16\%$

The residual ether solution gave the propane in the first fractions near 90° C. (9 mm.), which was purified (without recourse to oximation) by distillation, with B. P. 111°-112° C. (31¼ mm., corr.), being **2-methyl 3(2-methoxy phenyl) propane, (Prep. No. 25),** colorless, with an unpleasant odor of the kerosene type.

Analysis: Calculated for $C_{11}H_{16}O$ $C = 80.44\%$ $H = 9.81\%$
Found: $C = 80.34\%$ $H = 9.77\%$

The next fraction, near 130° C. (6 mm.) was oximated to remove aldehydes, there being little of such aldehydes present

since very little residual oxime was observed. The saturated alcohol was thereby obtained, **alpha-methyl 2-methoxy dihydrocinnamic alcohol (Prep. No. 19),** as a colorless, viscous liquid, odorless. B. P. 131½°-132½° C. (8¾ mm., corr.)

Analysis: Calculated for $C_{11}H_{16}O_2$ C = 73.29% H = 8.94%
Found: C = 72.95% H = 8.82%

There was a residue, about ¼ of the total, after the fraction of the reduction products containing the alcohol.

Reduction of alpha-ethyl 2-methoxy cinnamic aldehyde. Aldehyde 20 gms., alcohol 150 cc. of 95%, water 30 cc., gum solution 10 cc., catalyst 10 cc., the mixture absorbing approximately 1 mole of hydrogen at an average pressure of 2½ atmos. The reduction products, treated as before, gave out a bisulphite compound slowly from which the pure saturated aldehyde was obtained. This aldehyde, **alpha-ethyl 2-methoxy dihydrocinnamic aldehyde (Prep. No. 13)** distilled at 144°-145° C. (16 mm., uncorr.), having a dull sweet odor, colorless liquid.

Analysis: Calculated for $C_{12}H_{16}O_2$ C = 74.95% H = 8.39%
Found: C = 74.70% H = 8.64%

The ether filtrate, treated as before, gave mostly unchanged aldehyde after the first fractions near 100° C. (9 mm.). These first fractions, redistilled, gave the propane, **2-ethyl 3(2-methoxy phenyl) propane (Prep. No. 26)** as a colorless, mobile oil of B. P. 100½°-102½° C. (9 mm., corr.) with a slightly unpleasant kerosene odor.

Analysis: Calculated for $C_{12}H_{18}O$ C = 80.83% H = 10.19%
Found: C = 80.27% H = 10.37%

The portion near 135° C. (6 mm.) was found to be nearly all unchanged aldehyde, but a little of the saturated alcohol was obtained at 132°-134° C. (5½ mm., corr.). The residual oxime crystallizing. This **alpha-ethyl 2-methoxy dihydrocinnamic alcohol (Prep. No. 20)** was a colorless, odorless, liquid.

Analysis: Calculated for $C_{12}H_{18}O_2$ C = 74.17% H = 9.35%
Found: C = 74.17% H = 9.43%

In this instance the saturated alcohol was lower in yield than the propane, a residue being obtained. This fact is referred to again in Section B.

The reduction of alpha-amyl cinnamic aldehyde. With the same proportions as in the reduction of alpha-ethyl cinnamic aldehyde referred to above, a 1.6 mole reduction product of the aldehyde was treated with acetic anhydride and sodium acetate (34 gms. product, 100 gms. acetic anhydride, 3 gms. anhydrous sodium acetate refluxed for 45 minutes and worked up) gave the main portion at 134°-135° C. (3½ mm., uncorr.) which was the acetate of alpha-amyl dihydrocinnamic alcohol.
Analysis, the acetate:

Calculated for $C_{16}H_{24}O_2$	C = 77.36%	H = 9.74%
Found:	C = 77.85%	H = 9.82%

The alcohol was obtained from this by hydrolysis with 5% alcoholic potassium hydroxide after one hour on the water bath, as a colorless, viscous liquid, boiling at 119°-120° C. (2½ mm., uncorr.).

Analysis of this **alpha-amyl dihydrocinnamic alcohol (Prep. No. 15):**

Calculated for $C_{14}H_{22}O$	C = 81.48%	H = 10.76%
Found, from a dried but not distilled product from the acetate	C = 81.0%	H = 10.8%
Found, as prepared above from the acetate	C = 81.68%	H = 10.54%

From a one mole reduction product of the aldehyde treated for dinitrobenzoyl ester, a reddish product was obtained which was separated by its small solubility, a liquid, which was then hydrolyzed giving back a product which was impure alcohol (H = 10.56%) with no sign of unsaturated alcohol, a test with bromine being perhaps more significant than the analysis.

From the first fractions of many reduction products, in the same way as before, the propane, **2-amyl 3-phenyl propane (Prep. No. 21)** was obtained as a colorless mobile oil with an odor of

mixed lemon and kerosene type, collecting from 128°-130° C. (16 mm., uncorr.) and giving trouble in analysis like the previous hydrocarbon, for probably the same reason (see alpha-ethyl cinnamic aldehyde reductions).

Analysis: Calculated for $C_{14}H_{22}$ C = 88.34% H = 11.66%
Found: C = 86.95% H = 11.92%

Prep. (27) Alpha-ethyl cinnamic alcohol. Aluminum ethylate was found to be unsuitable in the preparation, but magnesium chlor-ethylate was found to be suitable ([39] gives an example of the same kind). 4 gms. of clean magnesium ribbon (in place of the fine filings formerly used) were added to a solution of hydrochloric acid, 5½ gms., in 100cc. of absolute alcohol, allowing the reaction to take place under reflux and finally bringing all the metal into solution by refluxing, free flame, for one hour or longer until no more metal is seen. A stream of nitrogen was passed through the mixture, the refluxing being continued, and 30 cc. of alpha-ethyl cinnamic aldehyde were added. The water in the condenser was not replenished, so that, on continued heating the top of the condenser soon attained a temperature of about 30° C. and in the course of seven hours about 40 cc. of solvent were carried off in the gas stream. The reaction mixture was then cooled and was thrown into excess of water. Acetic acid was added to facilitate extraction with ether, and the mixture extracted with ether, the whole, ether and mixture, filtered to remove a little resinous matter. The ether solution was then washed with sodium carbonate solution to remove acetic acid, then with water, dried, and the solvent removed. The residue was distilled (all distillations were done in nitrogen) at about 8 mm. pressure, giving 20 cc. of a slightly colored oil at 127°-137° C. (8 mm.), most at 137° C. and a thick residue beginning to decompose (from this residue a distillate near 200° C. (4mm.) gave C = 79.39% and H = 8.92%, suggesting dehydration in the low oxygen content). The first distillate gave on redistillation nearly all at 129°-130° C. (9 mm.), which is above 14° C. above the unsaturated aldehyde at that pressure, and the substance had

B. P. 131°-132° C. (9 mm., corr.). In the following, also, the non-admixture with unchanged aldehyde was a notable ameliorant in the preparation. The colorless product gave the following result on analysis for the unsaturated alcohol.

Analysis: Calculated for $C_{11}H_{14}O$ C = 81.42% H = 8.70%
Found: C = 81.28% H = 8.86%

A para-nitrobenzoyl ester gave H = 5.68% (calculated being 5.5% H) of M. P. 110°-111° C. (corr.) and a phenylurethane from phenylisocyanate (for 6 hours on the water bath in a sealed tube in mol. proportions), crystallizing on addition of petroether and melting at 62½°-63½° C. (63°-64° C. on correction) and not changing on crystallization from alcohol of 75%. The odor is slight and flowery like cinnamic alcohol. Decolorizes bromine solutions instantly on addition, with evolution of heat but no hydrobromic acid, the product being probably a liquid, and no color of bromine observable till near the point of saturation.

Prep. (28) Alpha-amyl cinnamic alcohol. As before, 4 gms. of magnesium ribbon in 5½ gms. of hydrochloric acid in 200 cc. of absolute alcohol, adding 30 cc. of alpha-amyl cinnamic aldehyde. After 4 hours of heating, the apparatus was left to cool overnight and the heating resumed next day to a total of 11½ hours. The gas stream carried over products reducing ammoniacal silver nitrate with production of a mirror. The product starts distilling at 144° C. (6 mm.) and was cut at 165° C. (6 mm.) being redistilled for collection at 141°-143° C. (5 mm., corr.), colorless, yield about 60%, faint odor, comparable to cinnamic alcohol.

Analysis: Calculated for $C_{14}H_{20}O$ C = 82.29% H = 9.88%
Found: C = 82.15% H = 10.0%

Phenyl urethane as before. Colorless M. P. 61°-62° C. (uncorr.). The alcohol is stable to repeated distillation at 172° C., reduced pressure.

Prep. (29) Alpha-methyl 4-methyl cinnamic alcohol. As before, magnesium 3½ gms., hydrochloric acid 5 gms. in 225 cc.

of absolute alcohol, adding 25 cc. of alpha-methyl 4-methyl cinnamic aldehyde, refluxing 7½ hours, no resin being formed requiring separation. Collected to 160° C. (10 mm.), redistilled to collect 142°-143° C. (11 mm., corr.) for analysis, colorless liquid, with an odor like the preceding, decolorizing dilute permanganate solution in water.

Analysis: Calculated for $C_{11}H_{14}O$ C = 81.42% H = 8.70%
Found: C = 81.39% H = 8.97%

Prep. (30) 3-4 methylene dioxy cinnamic alcohol ("cubebin"). As before, 4 gms. of magnesium, hydrochloric acid 5½ gms., absolute alcohol 225 cc., and 3-4 methylene dioxy cinnamic aldehyde 23 gms. Heat for 4 hours (a second experiment for two hours gave no better result, so the conditions need examination). On distillation to 200° C. (5 mm.) decomposition goes on rapidly, the alcohol being found in the distillate, collecting at 164°-165° C. (5 mm., uncorr.). Though the unchanged aldehyde would, if present, distill at 159°-160° C. in exactly the same conditions (by test) it is not present, since the distillate crystallizes pure white from benzene, without change of melting point when repeated from absolute alcohol, or dilute, giving a melting point at 78°-78¾° C. (corr.) (the correction of the thermometer for distillation should have been noted as 3° C. near 160° C., making the B. P. 167° C.).

Analysis: Calculated for $C_{10}H_{10}O_3$ C = 67.39% H = 5.66%
Found: C = 67.17% H = 5.95%

The yield is low (4 gms. impure). It reacts exactly like the others to bromine, permanganate solution, giving a benzoate from benzoyl chloride in pyridine and benzene on refluxing for 15 minutes, in a form easily distinguished from the alcohol, lower in density, long fine needles, M. P. 96°-97° C. (corr.), decolorizing bromine solutions slower than the alcohol.

Analysis: Calculated for $C_{17}H_{14}O_4$ C = 72.31% H = 5.00%
Found: C = 72.21% H = 5.22%

The impure phenyl urethane gave C = 68.45% (calc. 68.66%) by warming at 30° C. in a sealed tube the alcohol and phenyliso-

cyanate for 12 hours, M. P. near 95° C. The alcohol, catalytically reduced in the same circumstances as the unsaturated aldehydes in Section B, but with more catalyst, gave a 1 mole absorption in 10 minutes, and the resultant gave the unmistakable odor of the safrole type (dihydrosafrole present therefore), alpha-amyl cinnamic alcohol in the same circumstances giving the odor of the saturated propane previously described. The boiling point of the 3-4 methylene dioxy cinnamic aldehyde is given here for the first time, for comparison with the alcohol.

SECTION B.

An appendix discussing the residues on distillation of the reduction products, and their significance.

Concerning the residues, it is seen that they increase on repeated distillation (B17 and B10) and a quick distillation gives very little residue, such term applying to substances not distilling in the possible range for monomolecular products. Depolymerization seems to occur (B21) and the jump in the amount of residue by addition of an unsaturated alcohol to some distillates (B18) may be due to a steady polymerisation (or condensation, etc.) during the previous distillations. That dehydration occurs is probable from the analysis of residues (B12) and of more or less homogeneous bimolecular high boiling distillates that were occasionally obtained (B2), and they give evidence of changes also in their reducibility by this method, such reducible products not being obtained in the monomolecular products after reduction once. That the saturated alcohol is involved in the changes is shown by (B4) and (B5) where a portion on acetylation gave a large yield of the alcohol, a portion not so treated giving increasing residues; further in (B28) where the propane is greater in yield than the saturated alcohol. That the residues are due to pyrolysis is the conclusion from (B9) (B4) and (B5) where the amount of residue is very variable by variation of technique of isolation. That a mixture of monomolecular products can give residues is shown by (B19), but it is also shown that such residues ought to be small (B14) when the distillates are not contaminated. However, the isolated "pure" substances

are not exactly in the same state as the reduction products (traces of oxime, etc.) and the effects of traces of impurities cannot be gauged. The residues or bimolecular distillates gave no aldehyde or alcohol reactions and are postulated as ethers due to dehydration ([7] et al). The formation of bimolecular substances is, on these grounds, negatived and the same would be true for the unsaturated alcohols (B11) (B10) if it were not for the fact that the possibility of a "disproportionation" between unsaturated alcohol and saturated aldehyde, or vice versa, must be allowed, a possibility not to be neglected in a changing system through heat. The actual such effect must, however, be in general small, since the saturated aldehydes are mostly removed by treatment with sodium bisulphite before distillation. The test for unsaturated alcohols with bromine in carbon tetrachloride was highly useful since prepared mixtures of aldehydes and unsaturated alcohol, the latter in small quantities, gave ocular evidence of the presence of the unsaturated alcohol in the rapidity of decolorization and it is this test which is sometimes referred to in the phrase "giving no evidence of unsaturated alcohol."

EXPERIMENTAL (Section B)

B1. A mixed alcohol and acetic acid reduction of alpha-amyl 3-4 methylene dioxy cinnamic aldehyde, 1.2 moles hydrogen, no excess pressure, followed by bisulphite treatment. Distillate below 172° C. (3mm.) was .7 of the total. The distillate contained unchanged aldehyde. The residue (.3 of total) gave a fraction 175°-210° C. (3 mm.) (.1 of total) and a decomposing residue (.2 of total).

B2. A 1.1 mole aqueous-alcohol, no excess pressure, reduction of alpha-amyl cinnamic aldehyde, with bisulphite treatment, free flame distillations, gave .5 below 130° C. (5 mm.), containing mostly unchanged aldehyde at 160°-162° C. (16 mm.). Then .15 to 200° C. (4 mm.), then .20 at 212° C. (4 mm.) and .15 undistillable residue. The .20 fraction at 212°-215° C. (4 mm.) was redistilled and collected 200°-205° C. (3 mm.), a portion possibly homogeneous, which gave no aldehyde reactions, reacted with bromine approximately as for one ethylenic linkage in a bimolec-

ular compound, a molecular weight in acetic acid near 398 (a bimolecular saturated ether would be 398) and gave C = 85.95% H = 10.64% (such ether, one double bond, $C_{28}H_{40}O$ requires C = 85.6% and H = 10.3%). It absorbed hydrogen, catalytically as here in aqueous alcohol, as for one double bond in a bimolecular compound. The deliberate isolation of a similar product in other reductions could not be achieved and on repeating in larger quantities better results were prevented by continuing changes in the distillates.

B3. A 1.6 mole reduction, requiring repeated addition of catalyst, in aqueous alcohol, of alpha-amyl cinnamic aldehyde, no excess pressure, bisulphite treatment. Free flame, giving .2 from 125° to 130° C. (4 mm.) and .45 circa 130° C. (4 mm.), intermediate to 220° C. being .15 and residue .25. The first fractions on oximation gave 80% of an oxime at 142° to 146° C. (3 mm.) giving back unchanged aldehyde, the oxime not solidifying. The fraction at 130°-210° C. on redistillation goes over mostly at 210°-218° C. but leaves about .3 of the fraction as residue. On redistillation there is still a residue, the distillate decolorizing bromine as for one double bond in a bimolecular compound, not reacting with metallic sodium.

B4. A 1.6 mole, no excess pressure, aqueous alcohol reduction of alpha-amyl cinnamic aldehyde, repeated catalyst, with no bisulphite treatment. Distillation gave .15 to 120° C. (3 mm.) and .5 from 120°-150° C. (3 mm.) and .15 intermediate with .20 above 200° C., same pressure. This residue gave very little of the fraction around 212° C. (3 mm.), being mostly undistillable. What little there was near that temperature gave no evidence of reaction with phenyl isocyanate. A portion of the lower distillates, treated for dinitrobenzoyl ester (3, 5), led to the saturated alcohol only. Another portion treated for acetate led to the acetate of the saturated alcohol and the alcohol itself.

B5. A 1.6 mole, average 2½ atmos. pressure, aqueous alcohol reduction of alpha-amyl cinnamic aldehyde, no repeated catalyst, no bisulphite treatment, was treated without distillation for acetate. On distillation of the acetylated product .32 came over

to 128° C. (3 mm.), most at 110° C. and then .62 up to 140° C., nearly all at 132°-134° C. (3½ mm.) which is acetate of the saturated alcohol. The residue was .06. The middle and low fractions gave a total of .7 of acetate with a little hydrocarbon (the propane). The alcohol therefrom, with test for unsaturation gave no evidence at all of the unsaturated alcohol.

B6. A two mole reduction of alpha-ethyl cinnamic aldehyde, average pressure 2 atmos. aqueous alcoholic, repeated catalyst, bisulphite treatment, gave a .3 residue from which .1 was obtained at 165°-190° C. (2½mm.), absorbing bromine, and an undistillable residue of .2 of the total.

B7. 3 gms. of alpha-amyl dihydrocinnamic alcohol mixed with 6 gms. of alpha-amyl cinnamic aldehyde all distilled over, free flame, near 152° C. (10 mm.). Repeated, same result. The saturated hydrocarbon being added, the same result was observed on distillation. 1 gm. of alpha-ethyl dihydrocinnamic aldehyde was then added, giving the same distillation. Adding 1 gm. of cinnamic alcohol no difference was observed on distillation once more.

B8. An acetic acid reduction of alpha-amyl cinnamic aldehyde gave no evidence of acetate in the reduction products, test ing by hydrolysis with alkali.

B9. A 1.0 mole reduction of alpha-amyl cinnamic aldehyde, aqueous alcoholic, under pressure. One part was treated with bisulphite solution and gave a residue of .15. Another part without such treatment gave a residue of .07 in exactly the same circumstances of distillation.

B10. A 0.9 mole aqueous alcoholic reduction of alpha-amyl cinnamic aldehyde, no bisulphite treatment, no excess pressure but repeated catalyst and finally washing the reduction products in ether solution with sodium carbonate solution. A portion gave a residue of .1 over 150° C. (2 mm.) which was increased to 1.3 on repetition of distillation. These distillates were treated with bisulphite solution for one day and worked up in the usual manner as before, then heated in an oil bath at 150° C. for one hour,

finally distilling. Of these products .75 was distillate and .25 was residue comparable to all the previous ones. From distillates of B8 and B9 the fractions near 140° C. (3 mm.) were cut to test for unsaturated alcohol which might be expected about that point. However, they absorbed bromine only slowly and to a small extent. Distillates near 212° C. (3 mm.) from the residues were treated for ester, giving no evidence of reaction and the product distilled as if unchanged (giving as usual a residue), absorbing about the same amount of bromine as usual for that fraction (see B2).

B11. The same as B10, but under pressure. Treated directly for 3, 5 dinitrobenzoyl ester, the more soluble portions removed by treatment with aqueous alcohol and finally alcohol, separating by the greater density of the ester, gave a liquid ester from which only saturated alcohol could be obtained on hydrolysis with alcoholic potassium hydroxide, the residues decolorizing bromine solution in carbon tetrachloride to a slight extent.

B12. A 1.6 mole reduction, aqueous alcoholic, repeated catalyst, of alpha ethyl cinnamic aldehyde, average pressure 2½ atmos. Treated two days with bisulphite and the bisulphite compound removed. The remainder on distillation gave .5 below 150° C. (9 mm.) and a residue .5. The residue gave no reaction with phenyl hydrazine, absorbing bromine with no evolution of hydrobromic acid observed. Treated with benzoyl chloride in pyridine for benzoate the resultant absorbed bromine to the same extent as the original residue and gave no evidence of having been changed. The residue also gave no evidence of reaction with phenyl isocyanate, and analyses C = 84.1% and H = 9.6%, the hydrogen content being near that for an ether and the carbon low, and once more showing the residues too low in oxygen for an unchanged product.

B13. This residue in B12 gave no reaction with metallic sodium either alone or in benzene solution, with or without warming on the water bath.

B14. 15 gms. of alpha-ethyl cinnamic aldehyde, 15 gms. of alpha-ethyl dihydrocinnamic aldehyde, 15 gms. of alpha-ethyl

dihydrocinnamic alcohol distilled in an air bath gave no residue at 10 mm. pressure. Adding 15 gms. of alpha-ethyl cinnamic alcohol, the distillation was also complete. Standing one day, the distillation went on as before without residue.

B15. A reduction product as in B12 distilled in an oil bath with no bisulphite treatment gave.9 of distillate and .1 of residue, over 160° C. (9mm.).

B.16. Some of the reduction product in B15 was re-reduced to a 1.3 mole reduction and then treated as in B15. Residue was .15 and distillate .85, so that further reduction did not materially affect the residue formation.

B17. Some distillates from B15 were re-distilled and the residue increased to the proportion .2 of residue to .8 of distillate.

B18. These final distillates of B16 and B17 (15 gms.) were mixed with 5 gms. of alpha-ethyl cinnamic alcohol and distilled at 12 mm., free flame, the residue above 160° C. (12 mm.) being 4 gms. and at 16 mm. in a larger flask being 6 gms. (the residue being always that above the boiling points of any possible monomolecular products where not specified in temperature).

B19. 15 gms. of alpha-ethyl dihydrocinnamic alcohol, 15 gms. of alpha-ethyl cinnamic alcohol, mixed, distilled free flame at 18 mm. No residue. 7 gms. of alpha-ethyl dihydrocinnamic aldehyde added. Distilled, no residue. Added a minute crystal of sodium bisulphite. Distilled, residue 5 gms.

B20. A 1½ mole reduction product of alpha-ethyl cinnamic aldehyde, one half being treated with bisulphite and distilled, free flame. Residue 5 gms. and distillate 9 gms. The other half was not treated with bisulphite. Distilled in an oil bath at 11 mm., nearly all over at 122° C., leaving a residue of 1½ gms. Repeat distillation in an oil bath, residue mounted to 2½ gms.

B21. Some collected residues of distillations of reduction products of alpha-ethyl cinnamic aldehyde gave .6 near 190° C. (4 mm.), the remainder decomposing. The distillates redistilled gave a first portion, then a collected portion 196°-230° C. (5

mm.) and a residue undistillable. The collected portion on redistillation gave an appreciable first portion below 160° C. (5 mm.) and again a residue. On repetition with the portion of these last distillates near 200° C., the same behavior of giving a first fraction far below, and a residue, was observed and over 90% of the substance was rejected without amelioration of the process, pointing to splitting and polymerisation of some sort.

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